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Magnetic Studies on $(U,Y)O_{2+x}$ Solid Solutions

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Magnetic susceptibilities of $Y_yU_{1-y}O_{2+x}$ solid solutions with fluorite structure were measured from 4.2 K to room temperature. For the solid solutions with y values less than 0.50, an antiferromagnetic transition was observed. The Néel temperature decreased with decreasing uranium concentration, but in a different manner from that of $(U,Th)O_2$ or $(U,Zr)O_2$ solid solutions. The magnetic moment and Weiss constant were determined in the temperature range in which the Curie-Weiss law holds. With decreasing uranium concentration, the magnetic moment decreased more rapidly compared with those for $(U,Th)O_2$ and $(U,Zr)O_2$ solid solutions. The Weiss constant monotonously decreased with decreasing uranium concentration.

The oxidation state of uranium in the solid solutions was discussed by means of the magnetic susceptibility data for specimens with various x and y values. The substitution of Y^{3+} for U^{4+} in UO_2 proved to show the magnetic dilution effect with simultaneous oxidation of U^{4+} to U^{5+}.

The critical concentration for antiferromagnetism, C_0, for oxygen-stoichiometric solid solutions, $(U,Y)O_{2.0}$ was estimated to be 0.12. The Néel temperature of a hypothetical compound with fluorite structure in which all the cation sites are occupied by the U^{5+} ions, was estimated to be 15 K.

Introduction

Yttrium sesquioxide, Y_2O_3, well resembles uranium dioxide, UO_2, in crystal structure: The C-type rare-earth structure of Y_2O_3 is made up of removal of one-fourth oxygen from the fluorite structure of UO_2 in a regular manner. Formation of wide range of solid solution between Y_2O_3 and UO_2 may be related to the similarity of these crystal structures. Under proper reaction conditions, this solid solution takes gaseous oxygen into the crystal forming fluorite structure $(U,Y)O_2$. It would be meaningful to compare the magnetic properties of $(U,Y)O_2$ solid solutions with those of $(U,Th)O_2$ solid solutions (*1, 2*), because both Y_2O_3 and ThO_2 are diamagnetic. The substitution of Th^{4+} for U^{4+} in the UO_2 lattice caused a magnetic dilution, and the antiferromagnetic transition temperature has been found to decrease linearly with decreasing uranium concentration. In the case of $(U,Y)O_2$ solid solutions, however, the circumstances are a little more complicated. The substitution of Y^{3+} for U^{4+} in UO_2 lattice results in not only magnetic dilution of UO_2, but also oxidation of uranium ions to higher valence state in order to maintain the electrical neutrality in the solid solutions. Oxygen nonstoichiometry gives an additional effect on the magnetic properties by itself and through valence state change of the uranium ions.

Despite many investigations on phase relation and thermodynamics of UO_2–Y_2O_3

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system (*3–9*), the only magnetic study on this system has been done by Kemmler-Sack *et al.* (*10*). They measured the magnetic susceptibility of $Y_{0.5}U_{0.5}O_2$ solid solution in the temperature range from 84 to 473 K, and obtained the magnetic moment of U^{5+} from the Curie law by taking into account the temperature-independent paramagnetism.

In the present study, $Y_yU_{1-y}O_{2+x}$ solid solutions with various x and y values of which the crystal structure is fluorite type (same as UO_2) were prepared and their magnetic susceptibilities were measured from liquid helium temperature to room temperature. Change of magnetic moment, Weiss constant, and Néel temperature was examined to study the effect of Y^{3+} and excess or deficient oxygen on the magnetic properties of the solid solutions. Discussion was made on the oxidation state of uranium in the solid solutions on the basis of magnetic susceptibility data.

Experimental

1. Sample Preparation

UO_2 and Y_2O_3 were used as starting materials. Before use, UO_2 was reduced to stoichiometric composition in flowing hydrogen at 1000°C, and Y_2O_3 was heated in air at 850°C to remove any moisture.

The UO_2 and Y_2O_3 were weighed to the intended atom ratios of uranium and yttrium. After finely ground in an agate mortar, the mixtures were pressed into pellets and then heated under either of the following two conditions:

Condition I. The reaction in an induction furnace in flowing helium at 1450°C. The partial pressure of oxygen was approximately 1.0×10^{-1} Pa.

Condition II. The reaction in an SiC resistance furnace in flowing unpurified helium at 1380°C. The helium gas used here had the partial pressure of oxygen (approximately 10 Pa) significantly higher than that of Condition I.

After cooling to room temperature, the samples were crushed into powder, repressed and reacted under the same conditions as before to make the reaction complete. These procedures were repeated twice.

2. Analysis

2.1. X-ray diffraction analysis. X-ray diffraction study on the solid solutions was performed using Cu$K\alpha$ radiation with a Philips PW-1390 diffractometer with curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson-Riley extrapolation method (*11*) applied to the diffraction lines above 80° (2θ).

2.2. Determination of oxygen. The oxygen nonstoichiometry in the solid solutions was determined by the back-titration method (*12, 13*). The weighed amount of sample was dissolved in excess cerium(IV) sulfate solution. The cerium(IV) sulfate solution was standardized with stoichiometric UO_2. The excess cerium(IV) was titrated against standard iron(II) ammonium sulfate

TABLE I

LATTICE PARAMETER OF $Y_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS

Solid solution	Lattice parameter (Å)	Preparation condition
$Y_{0.05}U_{0.95}O_{2.003}$	5.4599	I
$Y_{0.10}U_{0.90}O_{2.002}$	5.4471	I
$Y_{0.15}U_{0.85}O_{1.997}$	5.4348	I
$Y_{0.20}U_{0.80}O_{1.995}$	5.4228	I
$Y_{0.25}U_{0.75}O_{1.991}$	5.4109	I
$Y_{0.30}U_{0.70}O_{1.989}$	5.3978	I
$Y_{0.35}U_{0.65}O_{1.973}$	5.3840	I
$Y_{0.40}U_{0.60}O_{1.959}$	5.3740	I
$Y_{0.45}U_{0.55}O_{1.946}$	5.3648	I
$Y_{0.50}U_{0.50}O_{1.892}$	5.3590	I
$Y_{0.55}U_{0.45}O_{1.865}$	5.3533	I
$Y_{0.40}U_{0.60}O_{2.009}$	5.3700	II
$Y_{0.50}U_{0.50}O_{1.970}$	5.3505	II

solution with ferroin indicator. The oxygen amount was determined for predetermined Y/U ratio.

3. Magnetic Susceptibility Measurement

Magnetic susceptibility was measured by a Faraday-type torsion balance in the temperature range from liquid helium temperature to room temperature. The apparatus was calibrated with Mn-Tutton's salt ($\chi_g = 10980 \times 10^{-6}/(T + 0.7)$) as a standard. The temperature of the sample was measured by a "normal" Ag vs Au-0.07 at.% Fe thermocouple and an Au–Co vs Cu thermocouple. Details of the experimental procedure have been described elsewhere (*2*).

Results and Discussion

1. Lattice Parameter

X-ray diffraction analysis showed that cubic solid solutions with fluorite structure were formed in single phase for all the specimens in this study. The composition and lattice parameter of the solid solutions prepared are listed in Table I. Figure 1 shows the variation of *O*/*M* ratio of solid solution $Y_yU_{1-y}O_{2+x}$ as a function of yttrium concentration, y, where M indicates Y+U. For the solid solutions prepared under Condition I, the *O*/*M* ratio decreases with the increase of y for $y > 0.3$, but below $y = 0.3$ the ratios are nearly two. Similar behavior has already been reported in earlier works on UO_2–Y_2O_3 system (*5*) and some rare-earth oxide–uranium oxide systems (*14–17*).

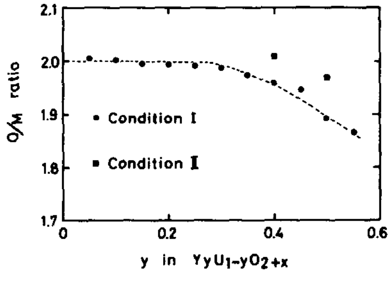

FIG. 1. Variation of *O*/*M* ratio with yttrium concentration.

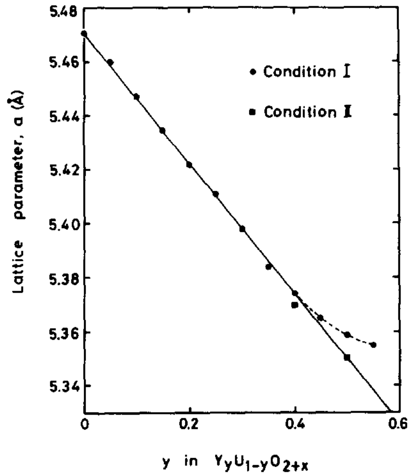

FIG. 2. Variation of lattice parameter with yttrium concentration. Solid line represents a (Å) = 5.4704–0.241y.

The variation of lattice parameter with yttrium concentration is shown in Fig. 2. The lattice parameter of the solid solutions decreases linearly with increasing yttrium concentration from that of UO_2 in the range of $0 \leq y \leq 0.3$. The variation of the parameter can be expressed by an equation, a (Å) = 5.4704 − 0.241y. In this equation, the term including the oxygen nonstoichiometry, x, was omitted since the absolute value of this term would be less than ~0.001; i.e., the coefficient of x is of the order of 0.1 (*18*), and $|x| \leq 0.011$ for the solid solutions with $y \leq 0.3$ (Table I).

2. Magnetic Susceptibility

The temperature dependence of magnetic susceptibilities per mole of uranium for the present solid solutions is shown in Figs. 3–5. For the solid solutions prepared under Condition I, an antiferromagnetic transition was found to occur in the y range below 0.50, and the Néel temperature, T_N, de-

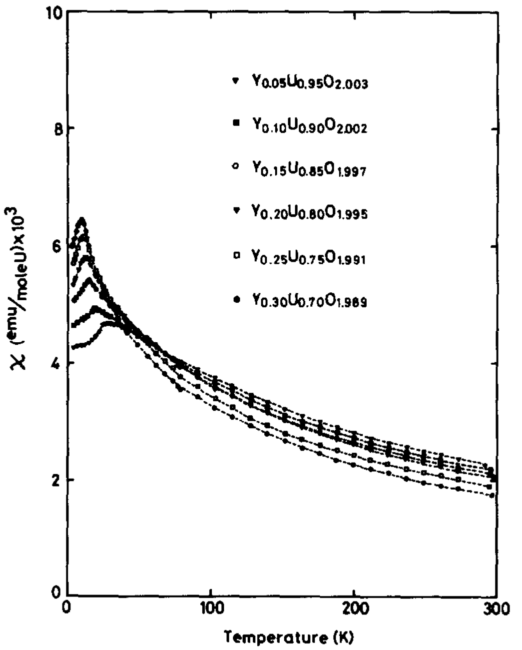

FIG. 3. Temperature dependence of magnetic susceptibility of $Y_yU_{1-y}O_{2+x}$ solid solutions with $y = 0.05$–0.30 prepared under Condition I.

creased with increasing yttrium concentration. At temperatures below T_N, the magnetic susceptibility considerably decreased with decreasing temperature. This is inconsistent with behavior of UO_2 (*19, 20*), (U,Th)O_2 solid solutions (*1, 2*), or (U,Zr)O_2 solid solutions (*21*) where the magnetic susceptibilities attained constant values below the Néel temperatures. In Fig. 3, the decrease of the magnetic susceptibility below T_N becomes prominent with yttrium concentration, which corresponds to the increased amount of U^{5+} ions as will be shown later. Since the constant magnetic susceptibility below T_N has been observed for the solid solutions in which the valence state of uranium is +4 only, the phenomenon that the magnetic susceptibility decreases monotonously below T_N may be due to magnetic interactions between U^{5+}–U^{5+} ions or in some cases those between U^{5+}–U^{4+} ions.

3. Valence State of Uranium

In Fig. 6 is plotted the mean valency of uranium calculated from the composition against yttrium concentration. Except for two points of $y = 0.50$ and 0.55, the data are seen on a smooth curve which increases with increasing yttrium concentration. The oxidation state of uranium in the solid solutions will be discussed by analyzing the magnetic properties obtained here in conjunction with the mean valency data for respective cases of oxygen nonstoichiometry and yttrium substitution.

3.1. Effect of nonstoichiometric oxygen. The oxygen nonstoichiometry in the solid solutions affects the effective magnetic moment of uranium mainly through the change of the valence state of uranium. This effect

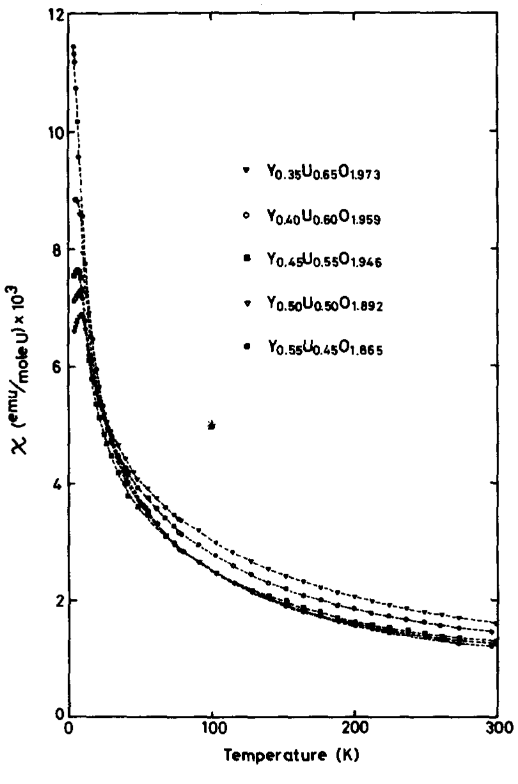

FIG. 4. Temperature dependence of magnetic susceptibility of $Y_yU_{1-y}O_{2+x}$ solid solutions with $y = 0.35$–0.55 prepared under Condition I.

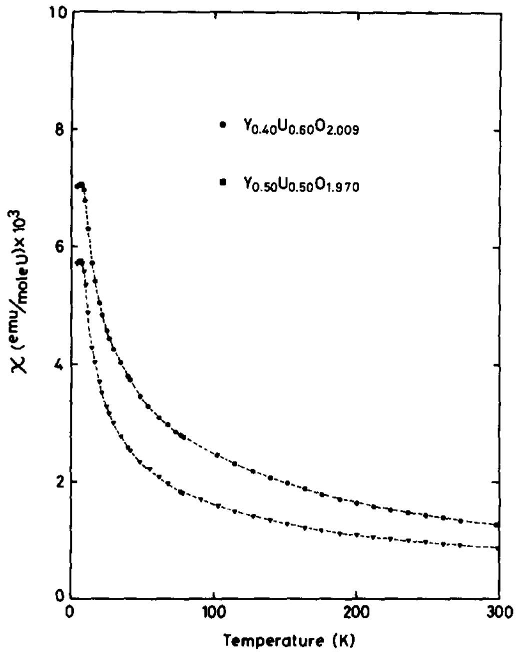

FIG. 5. Temperature dependence of magnetic susceptibility of $Y_yU_{1-y}O_{2+x}$ solid solutions prepared under Condition II.

will be analyzed for the solid solutions with the same y value but different x value.

If U^{4+} ions are assumed to be oxidized to U^{6+} state by the incorporation of oxygen and yttrium ions, the ionic species in the solid solutions are expressed as

$$Y_y^{3+}U_{1-x-1.5y}^{4+}U_{x+0.5y}^{6+}O_{2+x}^{2-}. \qquad (1)$$

In this case, the paramagnetic ion is U^{4+} only. The ratio of paramagnetic ion in the solid solution $Y_yU_{1-y}O_{2+x}$ decreases from $1 - y$ to $1 - x - 1.5y$. As will be shown later, the effective magnetic moment listed in Table II (μ_{eff}) is the one for a uranium ion. Then, the moment of U^{4+} ($\mu_{\mathrm{eff}}(U^{4+})$) is calculated from the relation, $\mu_{\mathrm{eff}}(U^{4+}) = \sqrt{(1-y)/(1-x-1.5\,y)}\,\mu_{\mathrm{eff}}$.

Let us consider solid solution $Y_{0.50}U_{0.50}O_{1.970}$, for example. The effective magnetic moment of U^{4+} was obtained to be 2.33 B.M. This value is by far smaller than the theoretical value for a U^{4+} ion in the crystalline field produced by eight oxygen ions in cubic symmetry. 2.83 B.M. (*22*), and further smaller than the one experimentally obtained for UO_2, 3.12 B.M. (*2, 23*). If solid solution $Y_{0.40}U_{0.60}O_{2.009}$ is chosen for another example, the moment of U^{4+} is calculated to be 2.49 B.M. This value is not appropriate for the moment of U^{4+}, either: The possibility of Eq. (1) should be excluded.

Next, the case that the oxidation of uranium proceeds from U^{4+} to U^{5+} will be considered. The ionic species in the solid solutions are then,

$$Y_y^{3+}U_{1-2x-2y}^{4+}U_{2x+y}^{5+}O_{2+x}^{2-}. \qquad (2)$$

In this case, both U^{4+} and U^{5+} ions contribute to the paramagnetism of solid solutions.

Consider the magnetic susceptibilities of two solid solutions with the same y value but different x values, viz., $Y_{0.40}U_{0.60}O_{1.959}$ and $Y_{0.40}U_{0.60}O_{2.009}$ which will be referred to as S.1 and S.2, respectively. The susceptibilities are

$$\chi(\mathrm{S.1}) = (1 - 2x_1 - 2y)\chi(U^{4+}) + (2x_1 + y)\chi(U^{5+}), \qquad (3)$$

$$\chi(\mathrm{S.2}) = (1 - 2x_2 - 2y)\chi(U^{4+}) + (2x_2 + y)\chi(U^{5+}), \qquad (4)$$

where $\chi(U^{4+})$ and $\chi(U^{5+})$ are the magnetic susceptibilities of U^{4+} and U^{5+}, respectively. By eliminating $\chi(U^{4+})$ from Eqs. (3) and (4), $\chi(U^{5+})$ is expressed as

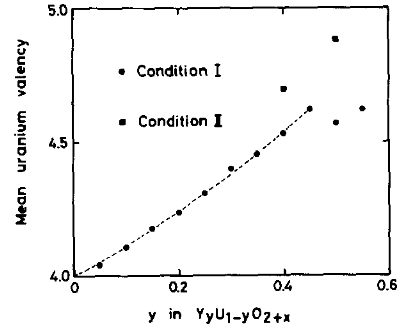

FIG. 6. Mean uranium valency against yttrium concentration.

$$\chi(U^{5+}) = \frac{1}{2(1-y)(x_1-x_2)} \times [(1-2x_2-2y)\chi(S.1) - (1-2x_1-2y)\chi(S.2)], \quad (5)$$

where χ(S.1) and χ(S.2) are given as magnetic susceptibilities per mole of $Y_yU_{1-y}O_{2+x}$, not per mole of uranium as given in Figs. 3–5. The reciprocal susceptibility of U^{5+} vs temperature curve is shown in Fig. 7. The Curie-Weiss law is found to hold in the temperature range from 50 K to room temperature and its effective magnetic moment was obtained to be 1.60 B.M. In the case that a U^{5+} ion is in the crystalline field produced by eight oxygen ions in cubic symmetry, the ground state $^2F_{5/2}$ (in Russel-Saunder's coupling scheme) splits into two levels, of which the lowest is quartet Γ_8 (in Bethe's notation) (*24*). If only this quartet level contributes to the paramagnetism of these solid solutions, their magnetic moment is calculated to be 2.00 B.M. (*25, 26*). The value obtained from the present experiments is a little lower than that calculated. However, such discrepancies have been observed sometimes in the uranates of alkaline earth elements with fluorite structure, MU_2O_6 (M = Ca, Sr, or Ba) (*27*). When Eqs. (3) and (4) are applied to the solid solutions, $Y_{0.50}U_{0.50}O_{1.892}$ and $Y_{0.50}U_{0.50}O_{1.970}$, the effective magnetic moment of U^{5+} is obtained to be 1.71 B.M., which is also reasonable for the magnetic moment of U^{5+}. For $Y_{0.50}U_{0.50}O_{1.970}$, the mean valency of uranium is +4.88 and its effective magnetic moment is obtained to be 1.74 B.M. by experiment. This slightly larger moment than 1.60 B.M. (1.71 B.M.) may be due to small amount of U^{4+} in the $Y_{0.50}U_{0.50}O_{1.970}$ solid solution.

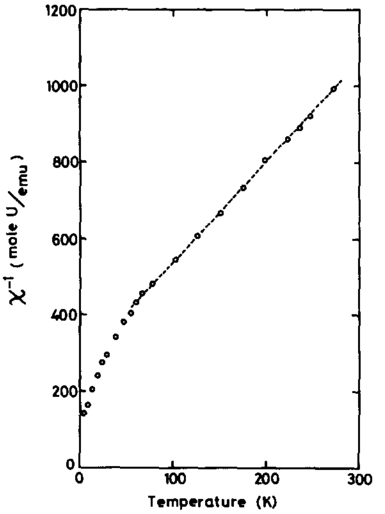

FIG. 7. Inverse magnetic susceptibility of U^{5+} ion vs temperature. Magnetic susceptibility of U^{5+} is calculated for fixed y solid solutions.

As the result of above considerations, it can be regarded that there exist U^{4+} and U^{5+} ions in the $Y_yU_{1-y}O_{2+x}$ solid solutions.

3.2. Effect of substitution of Y^{3+}. For analyzing the effect of Y^{3+} on the effective magnetic moment of uranium, solid solutions with the same x but different y value should be used as the most suited. These specimens were, however, not obtained, and the magnetic properties of $Y_{0.05}U_{0.95}O_{2.003}$ and $Y_{0.10}U_{0.90}O_{2.002}$, of which the x value was close to each other, were compared. There are additional reasons for this choice of the solid solutions as follows: (i) Since the O/M ratios are both close to two, the effect of oxygen nonstoichiometry is expected to be small enough to neglect. (ii) As the mean valencies of uranium are not very apart from +4, they are suited for studying the effect of Y^{3+} on U^{4+} without significant influence of uranium ions in higher valence state. (iii) Since the difference in uranium concentration is small, the difference in $\chi(U^{4+})$ or in $\chi(U^{5+})$ between the two solid solutions are also expected to be small.

For the solid solutions, $Y_{0.05}U_{0.95}O_{2.003}$ and $Y_{0.10}U_{0.90}O_{2.002}$ (to be referred to as S.3 and S.4 hereafter, respectively), the following two equations hold,

$$\chi(S.3) = (1-2x_3-2y_3)\chi(U^{4+}) + (2x_3+y_3)\chi(U^{5+}), \quad (6)$$

$$\chi(\mathrm{S}.4) = (1 - 2x_4 - 2y_4)\chi'(\mathrm{U}^{4+}) + (2x_4 + y_4)\chi'(\mathrm{U}^{5+}), \quad (7)$$

The prime in Eq. (7) refers to the different uranium concentration. However, the difference in Y^{3+} concentration is small for the above two solid solutions, so it was assumed as a first approximation that $\chi'(U^{4+})$ is equal to $\chi(U^{4+})$ and that $\chi'(U^{5+})$ is equal to $\chi(U^{5+})$. From Eqs. (6) and (7), the magnetic susceptibility of U^{5+} is expressed as

$$\chi(\mathrm{U}^{5+}) = \frac{1}{2(x_3 - x_4) + (y_3 - y_4) - 2(x_3y_4 - x_4y_3)} \times [(1 - 2x_4 - 2y_4)\chi(\mathrm{S}.3) - (1 - 2x_3 - 2y_3)\chi(\mathrm{S}.4)]. \quad (8)$$

By using the experimental susceptibilities for $\chi(S.3)$ and $\chi(S.4)$, the magnetic susceptibility of U^{5+} can be obtained, and its reciprocal susceptibility vs temperature curve is shown in Fig. 8. The Curie-Weiss law is found to hold in the temperature range from 22 K to room temperature, and the magnetic moment was obtained to be 1.38 B.M. This value is a little lower than 1.60 B.M. obtained in section 3.1 and further lower than 2.00 B.M. calculated for the U^{5+} ion in a crystalline field produced by the eight oxygen ions located at the corners of a cube (*25*, *26*). This difference may be from the approximation that $\chi(U^{4+}) = \chi'(U^{4+})$ and $\chi(U^{5+}) = \chi'(U^{5+})$.

TABLE II

MAGNETIC PARAMETERS FOR $Y_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS

Solid solution	Temperature range	C	μ_{eff} (B.M.)	θ (K)	T_N (K)
UO_2[a]	50 K–r.t.	1.217	3.12	−220.0	31.0
$Y_{0.05}U_{0.95}O_{2.003}$	35 K–r.t.	1.106	2.97	−192.1	24.5
$Y_{0.10}U_{0.90}O_{2.002}$	35 K–r.t.	1.028	2.87	−178.5	19.0
$Y_{0.15}U_{0.85}O_{1.997}$	20 K–r.t.	0.976	2.79	−166.8	15.1
$Y_{0.20}U_{0.80}O_{1.995}$	40 K–r.t.	0.935	2.73	−156.1	12.9
$Y_{0.25}U_{0.75}O_{1.991}$	30 K–r.t.	0.836	2.59	−144.1	10.8
$Y_{0.30}U_{0.70}O_{1.989}$	40 K–r.t.	0.743	2.44	−126.6	10.1
$Y_{0.35}U_{0.65}O_{1.973}$	40 K–r.t.	0.662	2.30	−117.4	8.9
$Y_{0.40}U_{0.65}O_{1.959}$	60 K–r.t.	0.601	2.19	−112.3	8.1
$Y_{0.45}U_{0.55}O_{1.946}$	50 K–r.t.	0.487	1.97	−90.9	7.2
$Y_{0.50}U_{0.50}O_{1.892}$	60 K–r.t.	0.462	1.92	−84.5	5.4
$Y_{0.55}U_{0.45}O_{1.865}$	60 K–r.t.	0.427	1.85	−90.4	—
$Y_{0.40}U_{0.60}O_{2.009}$	60 K–r.t.	0.503	2.01	−101.2	6.7
$Y_{0.50}U_{0.50}O_{1.970}$	75 K–r.t.	0.379	1.74	−135.0	6.6

[a] Parameters for UO_2 are given in Ref. (*2*).

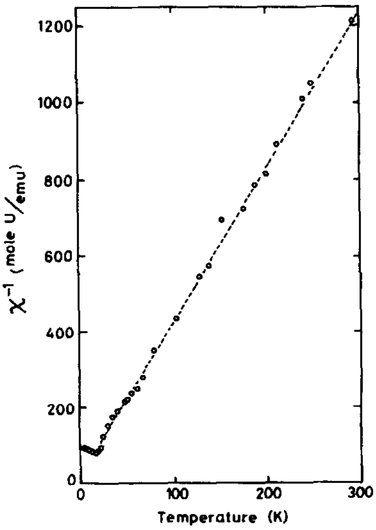

FIG. 8. Inverse magnetic susceptibility of U^{5+} ion vs temperature. Magnetic susceptibility of U^{5+} is calculated for nearly oxygen-stoichiometric solid solutions.

4. *Magnetic Moment*

From the reciprocal susceptibility vs temperature curves, the Curie-Weiss law was found to hold in the temperature ranges listed in Table II. The effective magnetic moment (μ_{eff}) and Weiss constant (θ) obtained in these temperature ranges are summarized in Table II. Figure 9 shows the variation of magnetic moment with uranium concentration, $C(= 1 - y)$. For comparison, the data of $(U,Th)O_2$ solid solutions (*2*) are also shown in this figure. In the ideal systems diluted magnetically, the magnetic moment in paramagnetic temperature region is unchanged irrespective of the concentration of paramagnetic ion, and the moment should be that for the isolated paramagnetic ion in a crystalline field produced by the anions around it. However, this does not hold sometimes. An example is for

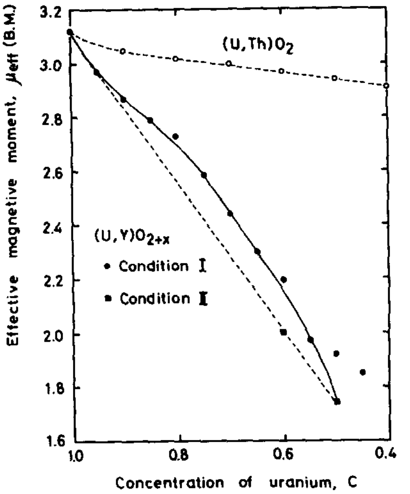

FIG. 9. Variation of effective magnetic moment with uranium concentration. Broken line connects the moments of UO_2 and $Y_{0.50}U_{0.50}O_{1.970}$.

Fe_2O_3–Al_2O_3 solid solutions (*28*, *29*) where the magnetic moment increased with ferric ion concentration. For (U,Th)O_2 or (U,Zr)O_2 solid solutions, the magnetic moment decreased with decreasing uranium concentration (*2*, *21*). The reason for this experimental fact was discussed in terms of the decrease of magnetic interaction with adjacent uranium ions as shown in the decrease of the Néel temperature (*2*). In (U,Y)O_2 solid solutions, the magnetic moment decreases to a greater degree than in (U,Th)O_2 or (U,Zr)O_2 solid solutions. This is considered to be due to the formation of U^{5+} which gives lower magnetic moment.

Assuming that there exists no magnetic interaction between uranium ions and that the magnetic moments of U^{4+} and U^{5+} are both independent of the concentration of uranium in the solid solutions, the magnetic moment of uranium for the solid solution in which the ratio of U^{4+} and U^{5+} is $(1-p):p$, is expressed as $\sqrt{(1-p)\mu(U^{4+})^2 + p\mu(U^{5+})^2}$, where $\mu(U^{4+})$ and $\mu(U^{5+})$ represent the magnetic moments of U^{4+} and U^{5+}, respectively. This value is larger than the arithmetic mean of the individual magnetic moments of U^{4+} and U^{5+}, $(1-p)\mu(U^{4+}) + p\mu(U^{5+})$. In the present solid solutions, the mean valency of uranium increases almost linearly with yttrium concentration as shown in Fig. 6. It reaches near +5 at $Y_{0.50}U_{0.50}O_{1.970}$. Therefore, the variation of magnetic moment with uranium concentration is expected to be convex upwards in μ_{eff} vs C curve. This is seen in Fig. 9. The solid line showing the experimental magnetic moments is higher than the straight broken line which connects the moments of UO_2 and $Y_{0.50}U_{0.50}O_{1.970}$.

The effect of oxygen nonstoichiometry can be examined for a pair of samples with the same y value but different x values, i.e., $Y_{0.40}U_{0.60}O_{2.009}$ and $Y_{0.40}U_{0.60}O_{1.959}$, as well as, $Y_{0.50}U_{0.50}O_{1.970}$ and $Y_{0.50}U_{0.50}O_{1.892}$. Smaller magnetic moments found for the solid solutions with larger x are consistent with the existence of the increased amount of uranium in U^{5+} state.

5. *Weiss Constant*

Figure 10 shows the variation of Weiss constant with uranium concentration for

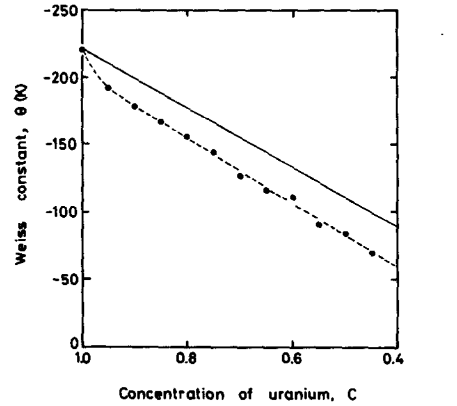

FIG. 10. Variation of Weiss constant with uranium concentration. Solid line represents the theoretical value calculated by assuming that the exchange interaction for any one U^{4+} ion is proportional to the number of nearest- and next-nearest-neighbor U^{4+} ions (see text).

the solid solutions prepared under Condition I. With decreasing uranium concentration, the Weiss constant decreases monotonously. The value is smaller than that calculated (straight solid line) by assuming that the exchange interaction for any one U^{4+} ion is proportional to the number of nearest- and next-nearest-neighbor U^{4+} ions (*2*). This fact can be explained by the formation of U^{5+} ions which gives generally smaller Weiss constant than U^{4+} ion. With decreasing uranium concentration, the departure from the linear relation obtained by the above calculation becomes larger, which indicates the formation of more U^{5+} ions in the solid solutions.

6. Néel Temperature and Critical Concentration of Antiferromagnetism

The problem of diluting a localized-moment type of magnetic materials with diamagnetic ions has been discussed by several researchers, and there exist some estimations on the critical concentration of antiferromagnetism (*30–36*). It has been pointed out that the critical concentration, C_0, of magnetic ions at which antiferromagnetism disappears is generally strongly dependent on the coordination number, Z, of the lattice, and independent of the spin S and the exchange integral, J, between nearest-neighbor spins (*30*). The result of theoretical works, however, cannot be directly applicable to the present system, for these works generally refer to the simple Heisenberg and Ising model of ferromagnet or antiferromagnet and do not deal with the superexchange interactions where the paramagnetic ions are largely distant each other and interact via such anions as oxygen intervening between them. We must take into account the superexchange interactions, because in the fluorite structure the nearest-neighbor actinide ions are in an unfavorable orientation for direct 5*f*–5*f* overlap (*37*). As will be shown later, the fact that the oxygen vacancies weaken the magnetic interactions between uranium ions is considered to indicate the superexchange type of interaction via oxygen ions. Further, in this system there exist two kinds of uranium valencies, U^{4+} and U^{5+}, both of which contribute to the paramagnetism and the ratio of U^{4+} and U^{5+} varies with uranium concentration.

The Néel temperature is given as a function of uranium concentration in Fig. 11. For comparison, the data of $(U,Th)O_2$ solid solutions (*2*) and $(U,Zr)O_2$ solid solutions (*21*) are plotted in the same figure. For $(U,Th)O_2$ and $(U,Zr)O_2$ solid solutions, the Néel temperature decreases linearly with decreasing uranium concentration and such behavior is qualitatively in accord with theoretical prediction (*30–36*) except near the critical concentration. By extrapolating a linear relation between T_N and $C(= 1 - y)$ for the samples of $0.5 \leq C \leq 0.7$ to $T_N = 0$ K (using the data of $Y_{0.50}U_{0.50}O_{1.970}$ as the T_N value for $C = 0.50$), the critical concentration for $(U,Y)O_{2.0}$ was estimated to be $C_0 =$

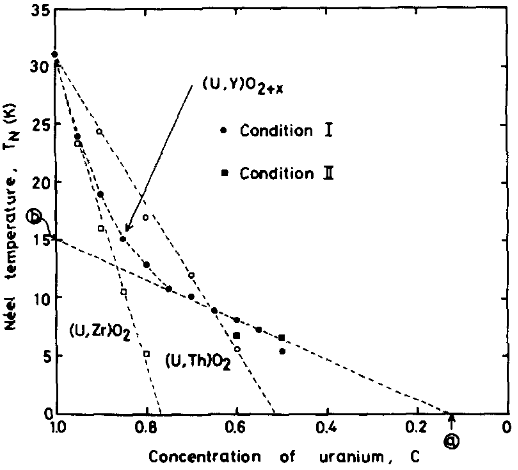

FIG. 11. Variation of Néel temperature with uranium concentration. Broken line for $Y_yU_{1-y}O_{2+x}$ solid solutions connects the data of oxygen-stoichiometric $(U,Y)O_{2.0}$. Point ⓐ represents the critical concentration of $(U,Y)O_{2.0}$. Point ⓑ represents the Néel temperature of the hypothetical compound with fluorite structure in which all the cation sites are occupied by the U^{5+} ions (see text).

0.12 (point ⓐ in Fig. 11). This concentration is close to the value, 0.136 (*35*), obtained by applying the series expansion of the mean cluster size to face-centered cubic lattice including up to the next-nearest-neighbor magnetic interactions.

Since the mean uranium valency of $Y_{0.50}U_{0.50}O_{1.970}$ is close to +5, the Néel temperature of the solid solutions of which the uranium concentration is around 0.5 may be regarded to reflect mainly the magnetic behavior of U^{5+} ions. Let us consider a hypothetical compound with fluorite structure in which all the cation sites are occupied by the U^{5+} ions. Its Néel temperature will be given by the extrapolation of T_N around $C = 0.5$ to $C = 1.0$ as shown in Fig. 11. The value obtained (ca. 15 K, point ⓑ) is lower than that of UO_2 (31.0 K) in which all the cation sites are occupied by the U^{4+} ions. This fact means that the Néel temperature for the paramagnetic ion with $S = \frac{1}{2}$ is lower than that for the paramagnetic ion with $S = 1$ in compounds with the same fluorite structure, which agrees with the theory that the magnetic exchange interaction is stronger for the compound with larger spin angular momentum (*38*).

7. *Effect of Oxygen Deficiency on Superexchange*

The $Y_yU_{1-y}O_{2+x}$ solid solutions with negative x values are not metal-interstitial, but anion-vacant as has been shown by density measurements (*4*).

By comparing the results of magnetic susceptibilities of two kinds of solid solutions with the same uranium concentration but different oxygen amounts, we can examine the effect of oxygen deficiency on the magnetic properties in antiferromagnetic region. The Néel temperature of $Y_{0.50}U_{0.50}O_{1.892}$ is lower than that of $Y_{0.50}U_{0.50}O_{1.970}$ by 1.2 K. The magnetic interactions of U^{4+} are stronger than those of U^{5+}, and the specimen $Y_{0.50}U_{0.50}O_{1.892}$ contains larger amount of U^{4+} than $Y_{0.50}U_{0.50}O_{1.970}$. Therefore, the above fact indicates that the oxygen deficiency of even 5.04 at.% (for $Y_{0.50}U_{0.50}O_{1.892}$) weakens the magnetic interactions between uranium ions considerably, which suggests that the oxygen ions at the anion sites in fluorite structure play an important role to transfer the interactions. On the other hand, the excess oxygens at interstitial sites have been found to weaken also the antiferromagnetic interactions between uranium ions (*19*, *26*). For instance, the Néel temperature of $Y_{0.40}U_{0.60}O_{2.009}$ is lower than that of $Y_{0.40}U_{0.60}O_{1.959}$, but we do not discuss the effect of excess oxygen closely, because it is difficult to separate this effect from that of U^{5+} in this system.

8. *Comparison of T_N Values with Those of (U,Sc)O_2 Solid Solutions*

It may be meaningful to compare the Néel temperatures of the present system with those of other systems. Since Y^{3+} and Sc^{3+} are both diamagnetic, by comparing the T_N values of the two solid solutions, $Y_yU_{1-y}O_{2+x}$ and $Sc_yU_{1-y}O_{2+x}$, an information concerning the influence of different magnetic diluent on the magnetic properties can be obtained. Table III shows the Néel temperatures of $Sc_{0.05}U_{0.95}O_{1.998}$ and $Sc_{0.10}U_{0.90}O_{2.001}$ which are nearly oxygen-stoichiometric (*26*). The Néel temperatures of (U,Sc)O_2 solid solutions are found to be lower than those of (U,Y)O_2 solid solutions for the specimens with the same uranium concentration in spite of smaller lattice parameters. In general, the magnetic ex-

TABLE III

MAGNETIC PARAMETERS FOR $Sc_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS

Solid solution	Lattice parameter (Å)	μ_{eff} (B.M.)	θ (K)	T_N (K)
$Sc_{0.05}U_{0.95}O_{1.998}$	5.4487	2.96	−207.0	24.0
$Sc_{0.10}U_{0.90}O_{2.001}$	5.4265	2.86	−190.2	17.2

change interaction becomes weaker with increasing the distance between magnetic ions. The above results, therefore, indicates that the lattice parameter or ionic separation is no longer an important factor in this case. This is the same as that obtained for $(U,Th)O_2$ and $(U,Zr)O_2$ solid solutions.

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